L7 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1989:141612 CAPLUS
DOCUMENT NUMBER: 110:141612
ORIGINAL REFERENCE NO.: 110:23265a,23268a
TITLE: Socks containing phthalocyanine derivatives as microbicides
INVENTOR(S): Kamimura, Masataka
PATENT ASSIGNEE(S): Earth Clean K. K., Japan; Daiwa Spinning Co., Ltd
SOURCE: Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63112701	A	19880517	JP 1986-255882	19861029

PRIORITY APPLN. INFO.: JP 1986-255882 19861029
OTHER SOURCE(S): MARPAT 110:141612

AB Socks contain metallic phthalocyanine and/or its derivs. I (M = metal; X = H or substituents) as microbicides which control growth of microorganisms in feet and socks and odors generated by the organisms. Cotton socks were treated with an alkali solution and soaked in a solution containing 1% by weight octasodium cobalt phthalocyanineoctcarboxylate for 5 h. The socks were then dried and tested for the deodorant activity.

IT Fungicides and Fungistats
(medical, phthalocyanine derivs. as, socks containing)

L7 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1995:356911 CAPLUS
DOCUMENT NUMBER: 122:125938
ORIGINAL REFERENCE NO.: 122:23383a,23386a
TITLE: Microbicides containing a phthalocyanine-iron derivative and an organic peroxide
INVENTOR(S): Myajima, Makoto; Ito, Masahiko; Shirai, Hiroyoshi
PATENT ASSIGNEE(S): Nippon Oils & Fats Co Ltd, Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 10 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 06321711	A	19941122	JP 1993-130126	19930507

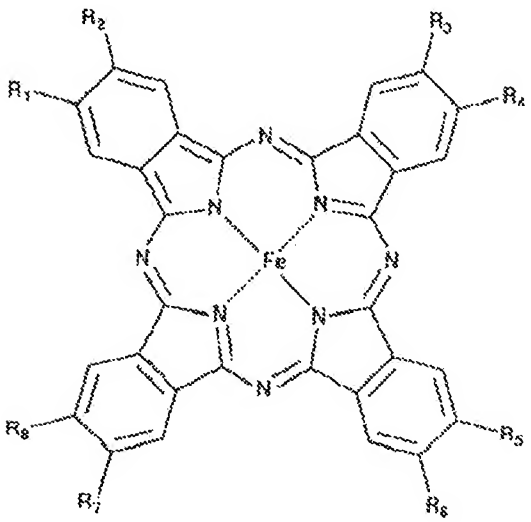
PRIORITY APPLN. INFO.: JP 1993-130126 19930507
OTHER SOURCE(S): MARPAT 122:125938

AB A microbicidal composition that is used in hospitals for sterilizing medical goods at low concentration and temperature, contains both (1) a phthalocyanine-iron derivative (I; ≥ 1 of R in R1-8 is carboxyl and the remaining Rs are H), and (2) an organic peroxide. For example, sterilizing effects of phthalocyanine-iron 8 carboxylic acid substituents and t-butylhydroperoxide were demonstrated.

IT Bactericides, Disinfectants, and Antiseptics
Fungicides and Fungistats
(microbicides containing phthalocyanine-iron derivative and organic peroxide)

CLAIM + DETAILED DESCRIPTION

[Claim(s)]
[Claim 1] General formula (1)
[Formula 1]



... (1)

It is the germicide which consists of phthalocyanine iron expressed with (one or more [in a formula and of R1-R8] is a carboxyl group, and others are hydrogen atoms), and organic peroxide.
[Claim 2] The sterilization method characterized by applying the phthalocyanine iron expressed with a general formula (1) by the substance, and organic peroxide.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a germicide and the sterilization method.

[0002]

[Description of the Prior Art] Like common knowledge, the sterilization which uses a germicide annihilates chemically the microorganism which adheres and exists in the inside of contrast, or contrast, and means vanishing the infection capability. As a germicide, oxidizing agents, such as aldehyde, such as surface active agents, such as halogenated compounds, such as alcohols, such as phenol derivatives, such as a saponated cresol solution, and ethanol, and crawl HEKISHIJIN, and reversed soap liquid, and formaldehyde, or hydrogen peroxide, etc. are used now. However, the germicide which demonstrates a bactericidal effect is not known by mixing organic peroxide and phthalocyanine iron.

[0003] The sterilization method of demonstrating a bactericidal effect is well-known by mixing conventionally the hemin and organic peroxide which are a kind of an iron complex. (Magnetic resonance, medicine, Vol.3, pp.96-101, :(1992) Arch.Biochem.Biophys., Vol.294, pp.55-63, (1992))

[0004]

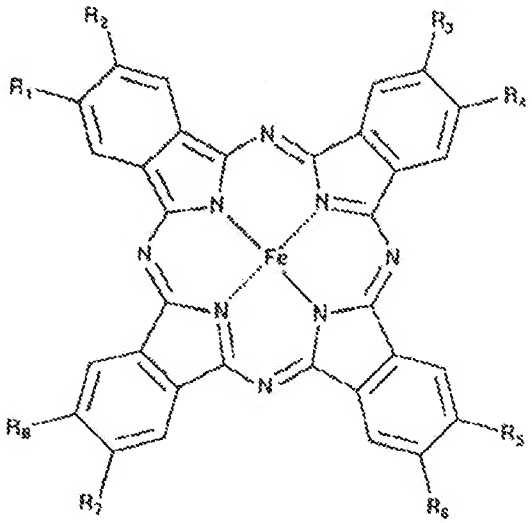
[Problem(s) to be Solved by the Invention] Low concentration and a powerful bactericidal effect are obtained for outstanding one of the conditions of a germicide. However, in the germicide used in the hospital etc. now, effective concentration is quite high. That is, a saponated cresol solution is used at 3%, and ethanol is used 70% by the concentration which formaldehyde was said as 1 to 5% 0.2 to 1%, and glutaraldehyde told 0.5 to 2% and to which reversed soap liquid said hydrogen peroxide for 1 to 10%, and crawl HEKISHIJIN as 1 to 3.5%, for example. Moreover, in a pathogenic microbe, many viable things exist also under low temperature, and it has been a problem in cold storage, such as an infusion solution. From this, an effective germicide is desired 4 degrees C generally used for refrigeration, and less than it. Compared with a room temperature, as for the glutaraldehyde liked and used in a hospital etc., sterilizing properties decline remarkably under low temperature. For example, in order to acquire an effect equivalent to a room temperature at 0 degree C, it is necessary to make concentration or sterilization time into 20 or more times. The purpose of this invention is to offer an effective germicide and the sterilization method under low concentration and low temperature.

[0005]

[Means for Solving the Problem] This invention is a general formula (1).

[0006]

[Formula 2]



... (1)

[0007] It is the sterilization method characterized by applying the phthalocyanine iron expressed with a general formula (1) by the germicide and substance which consist of phthalocyanine iron expressed with (one or more [in a formula and of R1-R8] is a carboxyl group, and others are hydrogen atoms), and organic peroxide, and organic peroxide.
[0008] The phthalocyanine iron which can be used by this invention is phthalocyanine iron which carries out coordination of the bivalence iron to the center of a mechanism, and has one or more carboxyl groups. Especially the phthalocyanine iron that has eight carboxyl groups in this is desirable. As for a phthalocyanine iron complex, it is desirable to use as a solution in a neutral or alkaline field. The solution containing various kinds of salts, such as others and various buffer solutions, a physiological saline, etc., can also be used for the diluent for adjusting the concentration of a phthalocyanine iron solution. [water /, such as tap water and sterilized water,]
[0009] As organic peroxide, for example Methyl-ethyl-ketone peroxide, cyclohexanone peroxide, 3, 3, 5-bird methyl SHIKUROHEKINOSAN peroxide, methylcyclohexanone peroxide, Peroxy ether, such as ketone peroxide, such as acetylacetone peroxide, Tert butylhydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, p-menthonaphtene hydroperoxide, 2, 5-dimethylhexane 2, 5-dihydroperoxide, Hydroperoxide, such as 1, 1, 3, and 3-tetramethyl BUCHIRUHIDORO peroxide, The 1 and 1-screws (t-butylperoxy) 3 and 3, 5-trimethylcyclohexane, 1 and 1-bis(t-butylperoxy) cyclohexane, 2, and 2-bis(t-butylperoxy) octane, 2 and 2-bis(t-butylperoxy) butane, G t-butyl peroxide, G t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy isopropyl) benzene, 2, the 5-dimethyl 2, dialkyl peroxide of 5-G (t-butylperoxy) hexyne 3 grade, diacetyl peroxide, JIISO butyryl peroxide JIOKU tile peroxide, didecanoyl peroxide, JIRAUROIRU peroxide, G (3, 3, 5-

trimethylhexanoyl) peroxide, succinic acid peroxide, Dibenzoyl peroxide, G (2, 4-dichlorobenzoyl) peroxide, Diacyl peroxide, such as G (m-toluoyl) peroxide, diisopropyl peroxi dicarbonate, G 2-ethylhexyl peroxi dicarbonate, G n-propyl peroxi dicarbonate, G millimeter still peroxi dicarbonate, G 2-ethoxyethyl peroxi dicarbonate, Peroxi dicarbonate, such as G methoxy isopropyl peroxi dicarbonate and Jl (3-methyl 3-methoxy butyl) peroxi dicarbonate, n-butyl 4, 4-bis(t-butylperoxy) valerate, t-butylperoxy acetate, t-butylperoxy iso butyrate, t-butylperoxy pivalate, t-butylperoxy neo decanoate, cumyl peroxy neo decanoate, t-butylperoxy-2-ethylhexanoate, t-butylperoxy 3 and 3, 5-trimethyl hexanoate, t-butylperoxy laurate, t-butylperoxy benzoate, G t-butylperoxy isophthalate, 2, the 5-dimethyl 2, 5-Jl (benzoyl peroxy) hexane, They are peroxy ester, such as t-butylperoxy maleate and t-butyl peroxyisopropyl carbonate, or acetyl cyclohexyl sulfonyl peroxide.

[0010] As for the germicide and the sterilization method of this invention, using in the following procedure is desirable. 0.05% or more of organic peroxide and concentration are mixed by making each solution adhere to a substance, a place, or an instrument etc. which sterilizes the phthalocyanine iron solution more than 10microM by methods, such as spraying and spreading, and concentration makes a bactericidal effect discover as a germicide. The goods polluted by the disease germ as the sterilization method, for example, a medical device, cookware, After concentration dips instruments, such as tableware, clothes, or an indoor portion in the phthalocyanine iron solution more than 10microM, the purpose is attained by adding the solution or suspension of organic peroxide so that the last concentration of organic peroxide may become 0.05% or more. Moreover, the same effect is acquired, even if it adds a phthalocyanine iron solution so that the last concentration of phthalocyanine iron may become more than 10microM after dipping in 0.05% or more of organic peroxide beforehand conversely. Furthermore, the same effect is acquired even if it mixes by making each solution adhere to these substances, a place, or an instrument by methods, such as spraying and spreading.

[0011] When phthalocyanine iron concentration is less than 10microM here, or when not filling organic peroxide concentration to 0.05%, a bactericidal effect is not fully acquired. Moreover, even if phthalocyanine iron concentration exceeds 100microM, there is no improvement in a bactericidal effect, and it is effective enough by the concentration not more than it respectively.

[0012]

[Effect of the Invention] According to the sterilization method of this invention, and the germicide, compared with the conventional sterilization method and a germicide, very effective sterilization under low concentration and low temperature can be performed.

[0013]

[Example] Test organism liquid was prepared as follows. That is, Staphylococcus aureus

(Staphylococcus aureus; Staphylococcus aureus) was suspended in the nutrient agar medium overnight after culture and in phosphate buffered saline (it abbreviates to PBS hereafter), and fungus liquid was adjusted by PBS so that number of microorganism might become 108 per ml.

[0014] Sterilization was performed as follows. 100microl The aqueous solution of 700microl, test organism liquid 100microl, and phthalocyanine iron was added for PBS to the sterilization test tube. After adding quickly 100micro of PBS suspension I of organic peroxide to this liquid and agitating for 10 seconds, it put gently for 30 minutes into the room temperature. After the examination of the bactericidal effect applied said 100micro of mixtures I to the brain trust heart infusion agar plate culture medium, it was cultivated at 37 degrees C for 15 to 24 hours, and it asked for the viable cell count from the formed colony count.

[0015] As an aqueous solution of work-example 1 phthalocyanine iron, 95.6microg/ml phthalocyanine iron 8 carboxylic acid (this [100microM iron phase]) was used, tert butylhydroperoxide PBS suspension was used as PBS suspension of organic peroxide, and it experimented according to the aforementioned method. Concentration of tert butylhydroperoxide was performed at 0 to 0.5% (the last concentration). The result was shown in Table 1. The viable cell count decreased or less to 1/1 million under existence of 0.05% or more of tert butylhydroperoxide.

[0016] Moreover, it experimented similarly except having added distilled water instead of the aqueous solution of phthalocyanine iron. The result was shown in Table 1. Unless it added phthalocyanine iron, the reduction in a viable cell count was not observed.

[0017]

[Table 1]

	フタロシアニン鉄	有機過酸化物		生菌数(cfu)
比較	フタロシアニン鉄8カルボン酸(100μM鉄)	t-ブチルヒドロペルオキシド(%)	0	1×10^{6}
			0.002	1×10^{6}
			0.005	1×10^{5}
			0.01	3×10^{3}
			0.02	1×10^{1}
本発明	フタロシアニン鉄8カルボン酸(100μM鉄)	t-ブチルヒドロペルオキシド(%)	0.05	$<1\times10^{0}$
			0.1	$<1\times10^{0}$
			0.2	$<1\times10^{0}$
			0.5	$<1\times10^{0}$
比較	−	t-ブチルヒドロペルオキシド(%)	0	1×10^{6}
			0.002	1×10^{6}
			0.005	1×10^{6}
			0.01	1×10^{6}
			0.02	1×10^{6}
			0.05	1×10^{6}
			0.1	1×10^{6}
			0.2	1×10^{6}
			0.5	1×10^{6}

[0018] As an aqueous solution of work-example 2 phthalocyanine iron, in addition, it experimented according to the aforementioned method so that the last concentration might become 0.1% about tert butylhydroperoxide as organic peroxide, so that concentration might be set to 0.2-100microM in phthalocyanine iron 8 carboxylic acid. The result was shown in Table 2. In the case where 0.1% of tert butylhydroperoxide is added, the reduction of the viable cell count depending on the concentration of phthalocyanine iron 8 carboxylic acid was checked. That is, under existence of phthalocyanine iron 8 carboxylic acid equivalent to the concentration of iron more than 20microM, the viable cell count decreased or less to 1/1 million.

[0019] moreover -- adding phthalocyanine iron 8 carboxylic acid (last concentration 0.2-100microM) as an aqueous solution of phthalocyanine iron -- instead of [of the aqueous solution of tert butylhydroperoxide] -- distilled water -- in addition, it experimented similarly. The result was shown in Table 2. The reduction in a viable cell count was not observed under

tert butylhydroperoxide nonexistence.

[0020]

[Table 2]

	フタロシアニン鉄		有機過酸化物	生菌数(ml^{-1})
比較	フタロシアニン鉄8カルボン酸（μM鉄）	0	t－ブチルヒドロペルオキシド(0.1%)	1×10^{5}
		0.5		1×10^{5}
		1		1×10^{5}
		2		1×10^{5}
		5		1×10^{5}
本発明	フタロシアニン鉄8カルボン酸（μM鉄）	10	t－ブチルヒドロペルオキシド(0.1%)	1×10^{2}
		20		$<1\times10^{0}$
		50		$<1\times10^{0}$
		100		$<1\times10^{0}$
比較	フタロシアニン鉄8カルボン酸（μM鉄）	0	－	1×10^{6}
		0.5		1×10^{6}
		1		1×10^{6}
		2		1×10^{6}
		5		1×10^{6}
		10		1×10^{6}
		20		1×10^{6}
		50		1×10^{6}
		100		1×10^{6}

[0021] As an aqueous solution of work-example 3 phthalocyanine iron, in addition, it experimented according to the aforementioned method so that the last concentration might become 1% about tert butylhydroperoxide as organic peroxide, so that concentration might be set to 0.2-100microM in phthalocyanine iron 8 carboxylic acid. The result was shown in Table 3. In the case where 1% of tert butylhydroperoxide is added, the reduction of the viable cell count depending on the concentration of phthalocyanine iron 8 carboxylic acid was checked.

That is, under existence of phthalocyanine iron 8 carboxylic acid more than 2microM, the viable cell count decreased or less to 1/1 million.

[0022] Moreover, as an iron complex, in addition, it experimented, according to the aforementioned method so that the last concentration might become 1% about tert butylhydroperoxide as organic peroxide, so that concentration might be set to 0.2-100microM in the aqueous solution of hemin. The result was shown in Table 3. In the case where 1% of tert butylhydroperoxide is added, when concentration of hemin was carried out to more than 5microM, the viable cell count decreased or less to 1/1 million.

[0023]

[Table 3]

	鉄錯体		有機過酸化物	生菌数(ml⁻¹)
比	フタロシアニン鉄	0	t－ブチルヒドロ	1×10^{5}
	8カルボン酸	0．2	ペルオキシド(1%)	1×10^{5}
較	(μM鉄)	0．5		1×10^{5}
		1		1×10^{5}
本	フタロシアニン鉄	2	t－ブチルヒドロ	$<1\times10^{0}$
	8カルボン酸	5	ペルオキシド(1%)	$<1\times10^{0}$
発	(μM鉄)	10		$<1\times10^{0}$
		20		$<1\times10^{0}$
明		50		$<1\times10^{0}$
	ヘミン	0	t－ブチルヒドロ	1×10^{5}
	(μM鉄)	0．2	ペルオキシド(1%)	1×10^{5}
比		0．5		1×10^{5}
		1		8×10^{4}
		2		5×10^{4}
		5		$<1\times10^{0}$
較		10		$<1\times10^{0}$
		20		$<1\times10^{0}$
		50		$<1\times10^{0}$
	ヘミン	0	－	1×10^{5}
	(μM鉄)	0．2		1×10^{6}
比		0．5		1×10^{6}
		1		1×10^{6}
		2		1×10^{6}
		5		1×10^{6}
較		10		1×10^{6}
		20		1×10^{6}
		50		1×10^{6}

[0024] Phthalocyanine iron 8 carboxylic acid of the quantity which is equivalent to the concentration M of 10micro as work-example 4 phthalocyanine iron was experimented according to the aforementioned method, using respectively methyl-ethyl-ketone peroxide of 0 to 1% of the last concentration as organic peroxide. The result was shown in Table 4.

Reduction in a viable cell count was checked by the concentration dependence target of methyl-ethyl-ketone peroxide, and the viable cell count decreased or less to 1/1 million under 0.05% or more of methyl-ethyl-ketone peroxide existence.

[0025] Moreover, according to the work example 4, it experimented except having added distilled water instead of the aqueous solution of phthalocyanine iron. The result was shown in Table 4. Unless it added phthalocyanine iron, the reduction in a viable cell count was not observed in less than 0.2% of methyl-ethyl-ketone peroxide.

[0026]

[Table 4]

	フタロシアニン鉄	有機過酸化物		生菌数(ml^{-1})
比較	フタロシアニン鉄8カルボン酸（10μM鉄）	メチルエチルケトンペルオキシド(%)	0	1×10^{6}
			0.002	1×10^{6}
			0.005	1×10^{6}
			0.01	1×10^{6}
			0.02	1×10^{5}
本発	フタロシアニン鉄8カルボン酸	メチルエチルケトンペルオキシド(%)	0.05	$<1\times10^{0}$
			0.1	$<1\times10^{0}$
			0.2	$<1\times10^{0}$
			0.5	$<1\times10^{0}$
比較	—	メチルエチルケトンペルオキシド(%)	0	1×10^{6}
			0.002	1×10^{6}
			0.005	1×10^{6}
			0.01	1×10^{6}
			0.02	1×10^{6}
			0.05	1×10^{5}
			0.1	1×10^{6}
			0.2	1×10^{5}
			0.5	1×10^{4}

[0027] As an aqueous solution of work-example 5 phthalocyanine iron, in addition, it

experimented according to the aforementioned method so that the last concentration might become 0.1% about methyl-ethyl-ketone peroxide as organic peroxide, so that concentration might be set to 0.2-100microM in phthalocyanine iron 8 carboxylic acid. The result was shown in Table 5. In the case where 0.1% of methyl-ethyl-ketone peroxide is added, the reduction of the viable cell count depending on the concentration of phthalocyanine iron 8 carboxylic acid was checked. That is, under existence of phthalocyanine iron 8 carboxylic acid equivalent to the concentration of iron more than 5microM, the viable cell count decreased or less to 1/1 million.

[0028] moreover -- adding phthalocyanine iron 8 carboxylic acid (last concentration 0.2-100microM) as an aqueous solution of phthalocyanine iron -- instead of [of the aqueous solution of methyl-ethyl-ketone peroxide] -- distilled water -- in addition, it experimented according to the work example 1. The result was shown in Table 5. The reduction in a viable cell count was not observed under methyl-ethyl-ketone peroxide nonexistence.

[0029]

[Table 5]

	フタロシアニン鉄	有機過酸化物	生菌数(個/ml)
比較	フタロシアニン鉄 0 8カルボン酸 0.5 (μM鉄) 1 2 5	メチルエチルケトンペルオキシド(0.1%)	1×10^{6} 1×10^{5} 1×10^{5} 1×10^{4} 1×10^{4}
本発明	フタロシアニン鉄 10 8カルボン酸 20 (μM鉄) 50 100	メチルエチルケトンペルオキシド(0.1%)	$<1\times10^{0}$ $<1\times10^{0}$ $<1\times10^{0}$ $<1\times10^{0}$
比較	フタロシアニン鉄 0 8カルボン酸 0.5 (μM鉄) 1 2 5 10 20 50 100	—	1×10^{6} 1×10^{6} 1×10^{5} 1×10^{5} 1×10^{6} 1×10^{6} 1×10^{5} 1×10^{6} 1×10^{6}

[0030] As an aqueous solution of work-example 6 phthalocyanine iron, in addition, it experimented according to the aforementioned method into 0 degree C so that the last concentration might become 0.02 to 1% about tert butylhydroperoxide as organic peroxide, so that concentration might be set to 100microM in phthalocyanine iron 8 carboxylic acid. The result was shown in Table 6. In the case where phthalocyanine iron 8 carboxylic acid of 100microM is added, the reduction of the viable cell count depending on the concentration of tert butylhydroperoxide was checked. That is, a reduction [Tsuguaki viable cell count] was checked under existence of 0.05% or more of tert butylhydroperoxide, and the viable cell count decreased or less to 1/1 million under existence of 0.2% or more of tert butylhydroperoxide.

[0031] Moreover, as a commercial germicide, glutaraldehyde (0.02 to 1% of the last concentration) was added, and it experimented similarly. The result was shown in Table 6. In order to decrease a viable cell count or less to 1/1 million, 0.5% or more of concentration was required.

[0032]

[Table 6]

	フタロシアニン鉄	有機過酸化物		生菌数(ml⁻¹)
比較	ﾌﾀﾛｼｱﾆﾝ鉄8ｶﾙﾎﾞﾝ酸(100μM鉄)	t-ブチルヒドロペルオキシド(%)	0	1×10^{6}
			0.02	1×10^{5}
本発明	フタロシアニン鉄8カルボン酸(100μM鉄)	t-ブチルヒドロペルオキシド(%)	0.05	3×10^{3}
			0.1	1×10^{3}
			0.2	$<1\times10^{0}$
			0.5	$<1\times10^{0}$
			1	$<1\times10^{0}$
比較	殺菌剤			
	グルタルアルデヒド(%)		0	1×10^{6}
			0.02	1×10^{6}
			0.05	1×10^{5}
			0.1	1×10^{5}
			0.2	2×10^{1}
			0.5	$<1\times10$
			1	$<1\times10^{0}$

[Translation done.]